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IV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE CUPRIANILINE ACETOBROMIDES.

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Presented June 9, 1894.

Recent investigations* have shown that double salts of cupriammonium containing two acids are easily obtainable in great numbers. It becomes a matter of interest to determine whether the substituted ammonias are capable of acting in the same way; and the present paper contains an account of the first experiments in this direction.

The only cupraniline compounds of which descriptions were found are three cuprosaniline compounds described by Saglier,† and cuprianiline chloride ($CuCl_2 2C_6H_7N$) described by Destrem.‡ Hence there was a wide field left open for the present investigation.

The compounds described in this paper are tabulated below.

(1.) $Cu(C_6H_7N)_2Br_2$.
(2.) $Cu(C_6H_7N)_2BrC_2H_3O_2$.
(3.) $Cu_8(C_6H_7N)_{16}Br_{15}(C_2H_3O_2)$.
(4.) $Cu_8(C_6H_7N)_{16}Br_{14}(C_2H_3O_2)_2$.
(5.) $Cu_8(C_6H_7N)_{16}Br_{13}(C_2H_3O_2)_3$.
(6.) $Cu_2(C_6H_7N)_4Br(C_2H_3O_2)_3$.
(7.) $Cu_8(C_6H_7N)_{16}Br(C_2H_3O)_{15}$.

Of these the simpler ones, Nos. 1 and 2, are undoubtedly definite compounds. Whether or not some of the others are isomorphous mixtures of these with cuprianiline acetate, which has not as yet been prepared in a pure state, it is hard to say.

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* Richards and Shaw, These Proceedings, XXVIII. 247; Richards and Whitridge, These Proceedings, XXX. 458; Richards and Oenslager, These Proceedings, XXXI. 78.

† Comptes Rendus, CVI. 1422.

‡ Bulletin de la Soc. Chim. de Paris, XXX. 482.

(1.) Cuprianiline Bromide, $Cu(C_6H_7N)_2Br_2$.

This compound is formed as a brown powder whenever cupric bromide is added to an alcoholic solution of aniline; but a much more beautiful crystalline preparation is obtained when the solution contains acetic acid. For example, three grams of cupric bromide were dissolved in about forty cubic centimeters of alcohol; and to this were added twenty cubic centimeters of acetic acid and fifteen cubic centimeters of aniline. The mixture turned green immediately, and beautifully brilliant brown crystalline flakes of cuprianiline bromide were deposited. Nothing could be easier than the preparation of this substance.

From analogy to the cupriammonium compounds, one would have expected the cuprianiline aceto-bromide to have been formed under conditions given above; but this is not the case unless the solution contains a large per cent of cupric acetate.

Among a great number of samples of cuprianiline bromide, which have all given satisfactory analytical results, at least four colors have been observed. A few preparations consisted of long glossy black crystals, others consisted of dark brown shining flakes. Yet others were of a lighter brown, and some were almost of a golden yellow. Possibly the difference was due to variations in the thickness of the individual crystals.

The new compound is insoluble in alcohol and glacial acetic acid. When mixed with water it is decomposed at once into a basic bromide of copper, aniline hydrobromide, and a little free aniline. Alkalies and acids of course decompose it.

In order to prepare the substance for the electrolytic determination of the copper it was treated with nitric acid, evaporated to dryness, and ignited. The residue was dissolved in a mixture of nitric and sulphuric acids; the former acid was expelled on the steam bath, and the copper was separated in the usual fashion. Bromine was determined as argentic bromide; and the aniline was calculated from the amount of carbon dioxide yielded by the combustion of the compound. As a final check upon the results, the nitrogen present was determined according to the method of Dumas.

Analyses of $Cu(C_6H_7N)_2Br_2$.

I. 0.1978 gram of the substance yielded 0.0308 gram of copper.
II. 0.2299 gram of the substance yielded 0.0357 gram of copper.

III. 0.2009 gram of the substance yielded 0.1842 gram of argentic bromide.
IV. 0.2530 gram of the substance yielded 0.2318 gram of argentic bromide.
V. 0.1028 gram of the substance gave 0.1313 gram of carbon dioxide upon combustion.
VI. 0.1705 gram of the substance yielded 10.20 cubic centimeters of moist nitrogen at 23° C. and 763.7 mm. pressure.

No.	Copper.	Bromine.	Aniline.	Nitrogen.
I. . .	15.57			
II. . .	15.52			
III. . .	—	39.02		
IV. . .	—	38.94		
V. . .	—	—	45.00	
VI. . .	—	—	—	6.77
Average	15.55	38.98	45.00	6.77

	Calculated for above Formula.	Found.
Copper	15.53	15.55
Bromine	39.04	38.98
Aniline	45.43	45.00
	100.00	99.53
Nitrogen	6.83	6.77

Many other similar determinations were made upon other samples, with similar results.

(2.) CUPRIANILINE ACETOBROMIDE, $Cu(C_6H_7N)_2(C_2H_3O_2)Br$.

This compound is formed with considerable difficulty, for the reaction tends to produce a compound containing either little or no acetic acid, or else little or no bromine. For the first time it was formed as follows. Three grams of cupric bromide were dissolved in about fifty cubic centimeters of alcohol, three grams of cupric acetate were dissolved in ten cubic centimeters of commercial acetic acid, with the addition of twenty cubic centimeters of water; the two solutions thus formed were mixed, and fifteen cubic centimeters of aniline were added to the mixture. In about half an hour fine brown crystals began to separate out, and these crystals proved to be cuprianiline acetobromide. Subsequently a great deal of time was expended in attempting to repeat this experiment, with continued failure. At last a few of the original crystals were sprinkled upon the surface of a mixture like the one just described, at the time when the crystals were expected; and a large mass of the long sought for substance immediately separated. The reasons of the inconsistency of the first success and the subsequent failures remains to be discovered. It is possibly connected with variations in temperature.

The new compound is nearly insoluble in alcohol and glacial acetic acid, and is partially decomposed by water. Potassic hydroxide removes all the bromine from it only with difficulty. It is easily broken up by concentrated nitric acid, but not until heat has been applied.

Because of the stability of the compound it was necessary to determine the bromine in a rather elaborate manner. The sample was intimately mixed with a large amount of sodic carbonate in a porcelain crucible, covered with a thick layer of the same salt, pressed down very thoroughly, and very gradually brought to a red heat. As the mass contracted, more sodic carbonate was sprinkled around the edges of the mixture, to prevent the escape of a trace of bromine. The fused mass was dissolved in hot water, and the sodic bromide was filtered off and determined as usual.*

Analyses of $Cu(C_6H_7N)_2C_2H_3O_2Br$.

I. 0.2100 gram of the first sample of substance yielded 0.0343 gram of copper upon electrolysis.

II. 0.1768 gram of the first sample of substance yielded 0.0860 gram of argentic bromide.

III. 0.1743 gram of the second sample of substance yielded 0.0866 gram of argentic bromide.

IV. 0.1232 gram of the second sample of substance yielded 0.0600 gram of argentic bromide.

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* This method was found to give the same results as that of Carius with these compounds. Of course the method would not answer if the bromine were directly combined with carbon.

	Calculated for above Formula.	Found. I.	II.	III.	IV.
Copper	16.38	16.33			
Bromine	20.70		20.70	21.14	20.80

(3.) OCTOCUPRIANILINE MONOACETOBROMIDE, $Cu_8(C_6H_7N)_{16}Br_{15}(C_2H_3O_2)$.

This substance has been made repeatedly as follows. Two grams of cupric bromide were dissolved in a hundred cubic centimeters of alcohol, and one and eight tenths grams of cupric acetate were dissolved in ten cubic centimeters of acetic acid, with the addition of just enough water to effect the solution. The two solutions were mixed, and fifteen cubic centimeters of aniline were added. In a quarter of an hour the desired crystals separated out from the deep green solution. The crystals resemble fine gunpowder in appearance, and possess properties more nearly resembling those of compound No. 1 than those of compound No. 2.

Analyses of $Cu_8(C_6H_7N)_{16}Br_{15}(C_2H_3O_2)$.

I. 0.1158 gram of the substance yielded 0.0181 gram of copper.
II. 0.1158 gram of the substance yielded 0.0996 gram of argentic bromide.
III. 0.2000 gram of the substance yielded 0.1738 gram of argentic bromide.
IV. 0.2712 gram of the substance yielded 0.2354 gram of argentic bromide.

	Calculated for $Cu_8(C_6H_7N)_{16}Br_{15}C_2H_3O_2$.	Found. I.	II.	III.	IV.
Copper	15.62	15.71			
Bromine	36.82		36.58	37.06	36.94

(4.) OCTOCUPRIANILINE TRIACETOBROMIDE, $Cu_8(C_6H_7N)_{16}Br_{13}(C_2H_3O_2)_3$.

Once this compound was obtained by adding 1.86 grams of aniline to a mixture of 2.23 grams of cupric bromide and 2.0 grams of acetic acid in alcoholic solution. The second time it was obtained by adding a few crystals of this first preparation to a mixture similar to that used for preparing No. 2, just as it was on the point of crystallization. The properties of this substance resemble very closely those of the last; and its analysis was conducted in the usual manner.

Analysis of $Cu_8(C_6H_7N)_{16}Br_{13}(C_2H_3O_2)_3$.

I. 0.1754 gram of the substance yielded 0.0278 gram of copper.
II. 0.1754 gram of the substance yielded 0.1318 gram of argentic bromide.
III. 0.2445 gram of the substance yielded 0.1865 gram of argentic bromide.
IV. 0.2200 gram of the substance yielded 0.1677 gram of argentic bromide.

	Calculated for	Found.			
	$Cu_8(C_6H_7N)_{16}Br_3(C_2H_3O_2)_3$.	I.	II.	III.	IV.
Copper	15.82	15.85			
Bromine	32.30		32.00	32.46	32.44

(5.) DICUPRIANILINE ACETOMONOBROMIDE, $Cu_2(C_6H_7N)_4Br(C_2H_3O_2)_3$.

This substance is formed with comparative ease, and was often obtained in the unsuccessful attempts to prepare cuprianiline acetobromide (No. 2). Its preparation is more certain if somewhat less cupric bromide — two grams instead of three — is used in the mixture described under that head. This variation of desirable conditions was to have been expected. Dicuprianiline acetomonobromide may also be formed by adding acetic acid to an alcoholic solution of cupric bromide until the color of the solution has become green, and then adding the aniline as before. After several hours, in either case, the compound separates as a dark bluish-black powder, insoluble in alcohol and glacial acetic acid. It is not decomposed by water, and boiling concentrated potassic hydrate will only remove a very small part of the bromine. At a moderate heat it is surprisingly stable; but upon ignition it is decomposed with considerable violence. When brought in contact with a drop of hot concentrated nitric acid it is almost explosive in the energy of its decomposition.

Analysis of $Cu_2(C_6H_7N)_4(C_2H_3O_2)_3Br$.

I. 0.1849 gram of the substance yielded 0.0310 gram of copper upon electrolysis.
II. 0.2310 gram of the substance yielded 0.0560 gram of argentic bromide.
III. 0.2053 gram of the substance yielded 0.0515 gram of argentic bromide.
IV. 0.1168 gram of the substance yielded 0.2026 gram of carbon dioxide upon combustion.

	Calculated for $Cu_2(C_6H_7N)_4Br(C_2H_3O_2)_3$.	Found. I.	II.	III.	IV.
Copper	16.82	16.77			
Bromine	10.57		10.32	10.69	
Carbon	47.61				47.31

(6.) OCTOCUPRIANILINE ACETOMONOBROMIDE, $Cu_8(C_6H_7N)_{16}Br(C_2H_3O_2)_{15}$.

This, the last compound on the list, is formed with great ease whenever a large excess of cupric acetate or acetic acid is added to cupric bromide in alcoholic solution and aniline is added to the mixture. It separates after about twenty-four hours as a fine bluish or brownish black powder, whose properties resemble very closely those of the previous compound.

Analysis of $Cu_8(C_6H_7N)_{16}Br(C_2H_3O_2)_{15}$.

I. 0.1540 gram of the substance yielded 0.0264 gram of copper upon electrolysis.

II. 0.5098 gram of the substance yielded 0.0338 gram of argentic bromide.

III. 0.3352 gram of the substance yielded 0.0212 gram of argentic bromide.

IV. 0.2117 gram of the substance yielded 0.0134 gram of argentic bromide.

V. 0.1983 gram of the substance yielded 0.3672 gram of carbon dioxide.

VI. 0.4346 gram of the substance yielded 28.8 cubic centimeters of moist nitrogen at 759.4 millimeters pressure and 23° C.

No.	Copper.	Bromine.	Carbon.	Nitrogen.
I. . . .	17.14			
II. . . .	—	2.82		
III. . . .	—	2.69		
IV. . . .	—	2.68		
V. . . .	—	—	50.51	
VI. . . .	—	—	—	7.46
Averages .	17.14	2.73	50.51	7.46

COMPOUND NO. 6.

	Calculated for $Cu_8(C_6H_5NH_2)_{16}Br(C_2H_3O_2)_{15}$.	Found.
Copper	17.18	17.14
Bromine	2.69	2.73
Carbon	51.04	50.51
Nitrogen	7.58	7.46

It is apparent that all the compounds described in this paper may be arranged in a series, based upon the formulæ so multiplied as to include eight molecules of the cuprianiline group $Cu(C_6H_7N)^{II}$. At one end of this list stands cuprianiline bromide, and at the other should stand cuprianiline acetate. Only six of the seventeen compounds necessary to fill out this scheme have been found: —

1. $Cu_8(C_6H_7N)_{16}Br_{16}$.
3. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)Br_{15}$.
4. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_3Br_{13}$.
2. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_8Br_8$.
5. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_{12}Br_4$.
6. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_{15}Br$.

These compounds exhibit a change in properties which corresponds to the progressive change in composition. The stability of the product and its difficulty of decomposition increases as the per cent of bromine decreases. The violence of the reaction with a drop of strong nitric acid increases in the same way. As the acetic acid increases and the bromine diminishes, the crystalline form becomes less and less evident, the first compound consisting of well marked crystals, and the last of an impalpable powder. The average color of the substance becomes blacker and bluer as one proceeds in the same direction. The preparation seems to depend upon two factors: in the first place, upon the relative proportions of cupric acetate and bromide taken at the start, and in the next place, upon the time required for the crystallization. When the conditions of temperature and dilution are such that crystallization takes place at once, a crystalline compound, rich in bromine, separates. When, on the other hand, many hours elapse before the substance appears, a powder very poor in bromine is formed. It is possible that the inversion temperature of these double salts may vary progressively, so that the use of a thermostat would be necessary to secure absolute certainty in the yield.

The possibility that most of these compounds might be mere mixtures has been already suggested; but it is evident that some at least must be definite compounds. The fact that in the case of Nos. 2 and 4 a few crystals of an earlier preparation were capable of starting the crystallization of the same substance in larger quantity, throws valuable light upon this point. The fact that most of the substances fit so closely into the series having eight atoms of copper as the basis seems to indicate a definite law; for the chances are decidedly against coincidence in this regard. The per cent of bromine is of course the best means of determining the agreement with the theory, and the agreement is very satisfactory. Each preparation appeared under the microscope to be perfectly homogeneous, so that if the substances are mixtures, the components must crystallize together.

From this series of compounds one would infer the possible existence of cuprianiline acetate, but many repeated trials to prepare this compound in a pure state ended in failure. Several different new compounds were obtained during this search, one of them probably having the formula $Cu_2(C_6H_7N)_3(C_2H_3O_2)_4$, for it contained 19.82 per cent of copper. Another compound, which consisted, like this last, of long light blue needles, contained only 19.10 per cent of copper; while two others, a brown and a black powder, contained respectively 21.80 per cent and 17.28 per cent. All of these compounds, together with others containing chlorine and iodine instead of bromine, and other substituted ammonias in place of aniline, will soon be investigated further at this Laboratory.